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(10) Energy-induced curable compositions.

- (11) A polymerizable composition comprising a polymerizable monomer at least one styrenic unsaturated monomer 2) at least two curing initiators and 3) an aromatic compound and an aromatic

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BIS(ACRYLIC-INDUCED CURABLE COMPOSITIONSField of the Invention

This invention relates to an energy-polymerizable composition comprising an allylically-unsaturated monomer, an epoxy monomer, or polyurethane precurser, and as curing agent a combination of an organometallic compound and an oxidizing agent; in another aspect, cured articles comprising the composition of the invention are disclosed. The compositions are useful, for example, as protective coatings, adhesives, and in graphic arts applications.

Background Of The Invention

Various photoinitiating curatives and initiators are produced in processes involving the use of organic solvents. There is an obvious effort by law makers, researchers, and industry, to promote high and 100% solids formulations to reduce or eliminate the use of such solvents and the attendant costs and environmental contamination. These processes require a latent catalyst or latent reaction promoter which can be activated as a concerted function.

Thermal curing of photopolymer precursters using reducing agents catalysts is known in the art (see for example U.S. Patent No. 4,521,565, and 4,502,581).

Photocuring of unsaturation polyurethane is well known (see T. A. Spachard, K.K.S. Huang, S.B. Lin, S.Y. Tsay, M. Kondo, Y.S. Ding, S.L. Cooper, "Adv. Polymer Science," 1986, 50, 647-680; C. Blasenbrey, "Photocuring of Unsaturated Polyurethane Precursters Using Diamine Curatives," 1981, 17, 83-93); photocuring of polyurethane precursters using diamine curatives is also known (see U.S. Patent Nos. 4,544,460, 4,540,945, and EP 20,803, German abstract). All of these methods suffer from one or more of the following disadvantages: sensitivity to oxygen, requirement of ultraviolet and/or high intensity light, the need for moisture removal, loss or dilution of urethane properties, low activity, poor stability, and poor pot-life.

The prior art discloses processes for the polymerization of epoxy materials. It is further known that a monosubstituted aromatic, such as an aromatic amine, can be used as a curing accelerator for epoxy materials (U.S. Patent No. 3,705,126 U.S. Patent No. 3,705,121, 3,714,005, 3,687,364 and 4,237,242 relate to the use of transition metal complexes as the activation between polyepoxides and polyfunctional curing additives, but they do not teach the polymerization of epoxide group-containing compositions not containing a curing additive. The polymerization of epoxide group-containing compositions is also known. Among such processes are those in which the polymerization catalyst is a substituted aromatic salt of a Lewis acid (e.g. diazobutonium salts) as described in U.S. Patent No. 3,794,570 and U.S. Patent No. 4,080,271; diazonium salts as is disclosed in U.S. Patent No. 4,026,705; and the organic salts of Group VIA elements, particularly the alkali metal salts, as is described in U.S. Patent No. 4,056,403; or a diazoxy chloride compound of a Group VIA-VB element as is disclosed in U.S. Patent No. 4,086,001. These compositions are intended to ultraviolet radiation for polymerization. Furthermore, the diazoxy chloride are monomer initiators.

U.S. Patent No. 4,216,286 relates to the thermal curing of cationically polymerizable compositions using organ salts and reducing agents.

Energy-polymerizable compositions comprising ionic salts of organometallic complex cations and carbon allylically-unsaturated monomers have been taught (see European Patent No. 19,551, 1984 004,914, 19103, German abstract; and 004,915, 1983, German abstract).

Neutral organometallic compounds have been used in combination with neutral halogenated compounds for the production of allylically-unsaturated monomers. (D. Smith, "Pure & Appl. Chem.", 53,511,165 (1981); H.M. Wagner, M.D. Pruznicki, "J. Photographic Science," 30, 230-236 (1982)).

The use of certain photoinitiating agents in combination with certain salts of polymerization of allylically-unsaturated monomers is also well known in the art. The technique has found applications in printing, halftone copying, and other imaging systems (see "Color in Light Sensitive Systems: Chemistry and Application of Radiation-Histo PhotoGraphic Processes," Wiley, New York, 1985, pp 156-158). Arylodonium salts have been previously described for use as photoinitiators in addition-polymerizable compositions

Summary of the Invention

- Briefly, the present invention provides an energy-polymerizable composition comprising 1) at least one allylically-unsaturated monomer, or 2) at least one epoxy monomer, or 3) polyurethane precurser, and as curing agent a combination of a organometallic compound and an amine salt. The compositions are useful as protective and decorative coatings, resins, adhesives, in restorative and aesthetic applications, and in imaging applications.
- What is not taught in the prior art, but what is taught in this invention, is the use of organometallic compounds in combination with certain salts for the photo- and electron beam-induced curing of allylically-unsaturated monomers, epoxy monomers or polyepoxide precursters, and the use of allylically-unsaturated monomers or polyurethane precursters.
- Advantages of compositions of the present invention when utilized in 100% solids coating compositions include:
- 1) An induced process initiation is disclosed that will reduce, eliminate, or eliminate the generation of induced solvent waste while reducing energy consumption.
 - 2) Radiation processing, particularly electron beam and photochemical curing, has generated capability for patterning and polymerizing thick and segmented coatings.
 - 3) More readily available monomers can be used in place of functionalized organics (see in the prior art) thereby resulting in lower viscosity and/or solutions which are easier to coat than more viscous organic solutions.
 - 4) Expanding the scope of curable monomers to include allylically-unsaturated monomers and epoxide precursters with specific properties.
 - 5) Increased flexibility in designing coatings via changing curing conditions.
 - 6) In this application, "energy-induced curing" means curing by means of conventional radiation (ultraviolet and visible) accelerated processes (including electron beam), and thermal (heating) and heat (heat) means.
 - 7) "Allylically-unsaturated monomer" means those monomers that polymerize by a free-radical mechanism.
 - 8) "Catalytically-active amount" means a quantity sufficient to effect polymerization of the curable composition to a polymerized product at least to a degree to create an increase in the viscosity of the composition.
 - 9) "Organic compound" means a chemical substance in which at least one carbon atom of an organic group is bonded to a metal atom ("Organic Chemistry", P.A. Coxon, G. Wilkinson, Wiley, New York, 1970, p. 487).
 - 10) "Polymer precurser" means a mixture of one or more monomers of the type including carboxylic acids and polyacrylates, and one or more monomers of the type including salts and polyesters bearing at least two anionic reactive hydrogen atoms may be substituted for carboxyl groups.
 - 11) "Substituted allyl group" means a hydrocarbon group substituted with one or more methyl or ethylene or vinylidene bonds.
 - 12) "Thickening agent" means a liquid that leads to two or more coats in the presence or absence of resinous binders.
 - 13) "Polymer salts" means an aliphatic or aromatic cationic cationic having 2 or more negatively charged groups.
 - 14) "Polymer" means an aliphatic or aromatic compound containing 2 or more polymerizable groups, and "cross-linked" means salts of dienes containing such as divinylbenzene, and styrene.

Detailed Description of the Invention

- The present invention provides, in a preferred embodiment, a photochemically-unsaturated composition comprising 1) at least one allylically-unsaturated monomer, or 2) at least one epoxy monomer, or polyurethane precurser, and a bicomponent curing agent mixture, and in a second embodiment a thermally-unsaturated composition comprising at least one allylically-unsaturated monomer or polyurethane precurser and a bicomponent curing agent mixture, the curing agent in all cases comprising

1. An organometallic compound having the structure

M

A

wherein M represents none or 1 to 12 ligands contributing p-electrons that can be the same or different selected from unsubstituted and unsaturated cyclic unsaturated compounds and groups and substituted and unsubstituted carborocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing 1 to 24 p-electrons to the valence shell of M;

10 A represents none or 1 to 24 ligands that can be the same or different contributing an even number of sigma electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M;

L₁ represents none, 1 to 12 ligands that can be the same or different, each contributing 0 no more than one sigma-electron each to the valence shell of each M;

M represents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups IVB, VIB, VIIB, and VIIIB (commonly referred to as transition metals);

15 L₁ and M are chosen so as to achieve a stable configuration; and

20 21 an organic salt curdling agent having the structure:

A_X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

U

V

X

Y

Z

W

There are restrictions on the total sum of electrons donated by the ligands, L₁, L₂, L₃ of formula I and the valence electrons generated by the metal. For most organometallic compounds, not involving intermolecular metal bonding, this sum is governed by the "valence electron rule" (see U.S. Patent No. 46,811 (1980)). This rule states that the most stable organometallic compounds tend to be those compounds in which the sum of the electrons donated by the ligands and the metal is eight. This skill in the art, however, knows that there are exceptions to this rule and that organometallic compounds having a sum of 16, 17, 18, and 20 electrons are also known. Therefore, organometallic compounds including intermolecular metal-metal bonding are described by formula I in which constitutional entities having a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell are included within the scope of an invention.

For compounds described in formula I in which intermolecular metal-metal bonding exists, some departure from the "valence electron rule" can occur. It has been suggested by Amer. Chem. Soc. (1972) and Sato (1976) that the departure from the "valence electron rule" is due to metal-ligand interactions involving the metal's valence shell electrons to cause some unavailability for ligand bonding. Hence, rules that count electrons around each metal separately in cluster, cluster valence electrons (CVE), and a intercluster compound having intercluster, intracluster, and extracluster geometry is seen to have 80, 92, or 94 CVEs, respectively. These stated in the art however, know that there are exceptions to this electron counting method, and that organometallic compounds have a sum of 42, 44, 46, 50 CVEs for a bimetallic compound and 58 CVEs for a trimetallic compound and 66 known. Therefore, cl. 11, or substituted organometallic compounds are described by formula I in which a complicated metal cluster, MM_n, MM_n, or MM_n has a total sum of 26, 42, 44, 46, 50, or 58 CVEs in the valence shell, respectively, and are included within the scope of this invention.

Illustrative examples of organometallic compounds according to formula I include:
 (CH₃COOC)₂Al
 (CH₃COO)₂Be
 (CH₃COOC)₂Li
 (CH₃COOC)₂Na
 (CH₃COOC)₂Rb
 (CH₃COOC)₂K
 (CH₃COOC)₂Cu(OH)₂
 (CH₃COOC)₂Zn(OH)₂
 (CH₃COOC)₂Fe(OH)₂
 (CH₃COOC)₂Cr(OH)₂
 (CH₃COOC)₂Co(OH)₂
 (CH₃COOC)₂Mn(OH)₂
 (CH₃COOC)₂Ni(OH)₂
 (CH₃COOC)₂FeCl₂
 (CH₃COOC)₂FeBr₂
 (CH₃COOC)₂FeI₂
 (CH₃COOC)₂FeCl₃
 (CH₃COOC)₂FeBr₃
 (CH₃COOC)₂FeI₃
 (CH₃COOC)₂Fe(OAc)₂
 (CH₃COOC)₂Fe(OAc)₃
 (CH₃COOC)₂Fe(OAc)₂·2H₂O
 (CH₃COOC)₂Fe(OAc)₃·2H₂O
 (CH₃COOC)₂Fe(OAc)₂·3H₂O
 (CH₃COOC)₂Fe(OAc)₃·3H₂O
 (CH₃COOC)₂Fe(OAc)₂·4H₂O
 (CH₃COOC)₂Fe(OAc)₃·4H₂O
 (CH₃COOC)₂Fe(OAc)₂·5H₂O
 (CH₃COOC)₂Fe(OAc)₃·5H₂O
 (CH₃COOC)₂Fe(OAc)₂·6H₂O
 (CH₃COOC)₂Fe(OAc)₃·6H₂O
 (CH₃COOC)₂Fe(OAc)₂·7H₂O
 (CH₃COOC)₂Fe(OAc)₃·7H₂O
 (CH₃COOC)₂Fe(OAc)₂·8H₂O
 (CH₃COOC)₂Fe(OAc)₃·8H₂O
 (CH₃COOC)₂Fe(OAc)₂·9H₂O
 (CH₃COOC)₂Fe(OAc)₃·9H₂O
 (CH₃COOC)₂Fe(OAc)₂·10H₂O
 (CH₃COOC)₂Fe(OAc)₃·10H₂O
 (CH₃COOC)₂Fe(OAc)₂·11H₂O
 (CH₃COOC)₂Fe(OAc)₃·11H₂O
 (CH₃COOC)₂Fe(OAc)₂·12H₂O
 (CH₃COOC)₂Fe(OAc)₃·12H₂O
 (CH₃COOC)₂Fe(OAc)₂·13H₂O
 (CH₃COOC)₂Fe(OAc)₃·13H₂O
 (CH₃COOC)₂Fe(OAc)₂·14H₂O
 (CH₃COOC)₂Fe(OAc)₃·14H₂O
 (CH₃COOC)₂Fe(OAc)₂·15H₂O
 (CH₃COOC)₂Fe(OAc)₃·15H₂O
 (CH₃COOC)₂Fe(OAc)₂·16H₂O
 (CH₃COOC)₂Fe(OAc)₃·16H₂O
 (CH₃COOC)₂Fe(OAc)₂·17H₂O
 (CH₃COOC)₂Fe(OAc)₃·17H₂O
 (CH₃COOC)₂Fe(OAc)₂·18H₂O
 (CH₃COOC)₂Fe(OAc)₃·18H₂O
 (CH₃COOC)₂Fe(OAc)₂·19H₂O
 (CH₃COOC)₂Fe(OAc)₃·19H₂O
 (CH₃COOC)₂Fe(OAc)₂·20H₂O
 (CH₃COOC)₂Fe(OAc)₃·20H₂O
 (CH₃COOC)₂Fe(OAc)₂·21H₂O
 (CH₃COOC)₂Fe(OAc)₃·21H₂O
 (CH₃COOC)₂Fe(OAc)₂·22H₂O
 (CH₃COOC)₂Fe(OAc)₃·22H₂O
 (CH₃COOC)₂Fe(OAc)₂·23H₂O
 (CH₃COOC)₂Fe(OAc)₃·23H₂O
 (CH₃COOC)₂Fe(OAc)₂·24H₂O
 (CH₃COOC)₂Fe(OAc)₃·24H₂O
 (CH₃COOC)₂Fe(OAc)₂·25H₂O
 (CH₃COOC)₂Fe(OAc)₃·25H₂O
 (CH₃COOC)₂Fe(OAc)₂·26H₂O
 (CH₃COOC)₂Fe(OAc)₃·26H₂O
 (CH₃COOC)₂Fe(OAc)₂·27H₂O
 (CH₃COOC)₂Fe(OAc)₃·27H₂O
 (CH₃COOC)₂Fe(OAc)₂·28H₂O
 (CH₃COOC)₂Fe(OAc)₃·28H₂O
 (CH₃COOC)₂Fe(OAc)₂·29H₂O
 (CH₃COOC)₂Fe(OAc)₃·29H₂O
 (CH₃COOC)₂Fe(OAc)₂·30H₂O
 (CH₃COOC)₂Fe(OAc)₃·30H₂O
 (CH₃COOC)₂Fe(OAc)₂·31H₂O
 (CH₃COOC)₂Fe(OAc)₃·31H₂O
 (CH₃COOC)₂Fe(OAc)₂·32H₂O
 (CH₃COOC)₂Fe(OAc)₃·32H₂O
 (CH₃COOC)₂Fe(OAc)₂·33H₂O
 (CH₃COOC)₂Fe(OAc)₃·33H₂O
 (CH₃COOC)₂Fe(OAc)₂·34H₂O
 (CH₃COOC)₂Fe(OAc)₃·34H₂O
 (CH₃COOC)₂Fe(OAc)₂·35H₂O
 (CH₃COOC)₂Fe(OAc)₃·35H₂O
 (CH₃COOC)₂Fe(OAc)₂·36H₂O
 (CH₃COOC)₂Fe(OAc)₃·36H₂O
 (CH₃COOC)₂Fe(OAc)₂·37H₂O
 (CH₃COOC)₂Fe(OAc)₃·37H₂O
 (CH₃COOC)₂Fe(OAc)₂·38H₂O
 (CH₃COOC)₂Fe(OAc)₃·38H₂O
 (CH₃COOC)₂Fe(OAc)₂·39H₂O
 (CH₃COOC)₂Fe(OAc)₃·39H₂O
 (CH₃COOC)₂Fe(OAc)₂·40H₂O
 (CH₃COOC)₂Fe(OAc)₃·40H₂O
 (CH₃COOC)₂Fe(OAc)₂·41H₂O
 (CH₃COOC)₂Fe(OAc)₃·41H₂O
 (CH₃COOC)₂Fe(OAc)₂·42H₂O
 (CH₃COOC)₂Fe(OAc)₃·42H₂O
 (CH₃COOC)₂Fe(OAc)₂·43H₂O
 (CH₃COOC)₂Fe(OAc)₃·43H₂O
 (CH₃COOC)₂Fe(OAc)₂·44H₂O
 (CH₃COOC)₂Fe(OAc)₃·44H₂O
 (CH₃COOC)₂Fe(OAc)₂·45H₂O
 (CH₃COOC)₂Fe(OAc)₃·45H₂O
 (CH₃COOC)₂Fe(OAc)₂·46H₂O
 (CH₃COOC)₂Fe(OAc)₃·46H₂O
 (CH₃COOC)₂Fe(OAc)₂·47H₂O
 (CH₃COOC)₂Fe(OAc)₃·47H₂O
 (CH₃COOC)₂Fe(OAc)₂·48H₂O
 (CH₃COOC)₂Fe(OAc)₃·48H₂O
 (CH₃COOC)₂Fe(OAc)₂·49H₂O
 (CH₃COOC)₂Fe(OAc)₃·49H₂O
 (CH₃COOC)₂Fe(OAc)₂·50H₂O
 (CH₃COOC)₂Fe(OAc)₃·50H₂O
 (CH₃COOC)₂Fe(OAc)₂·51H₂O
 (CH₃COOC)₂Fe(OAc)₃·51H₂O
 (CH₃COOC)₂Fe(OAc)₂·52H₂O
 (CH₃COOC)₂Fe(OAc)₃·52H₂O
 (CH₃COOC)₂Fe(OAc)₂·53H₂O
 (CH₃COOC)₂Fe(OAc)₃·53H₂O
 (CH₃COOC)₂Fe(OAc)₂·54H₂O
 (CH₃COOC)₂Fe(OAc)₃·54H₂O
 (CH₃COOC)₂Fe(OAc)₂·55H₂O
 (CH₃COOC)₂Fe(OAc)₃·55H₂O
 (CH₃COOC)₂Fe(OAc)₂·56H₂O
 (CH₃COOC)₂Fe(OAc)₃·56H₂O
 (CH₃COOC)₂Fe(OAc)₂·57H₂O
 (CH₃COOC)₂Fe(OAc)₃·57H₂O
 (CH₃COOC)₂Fe(OAc)₂·58H₂O
 (CH₃COOC)₂Fe(OAc)₃·58H₂O
 (CH₃COOC)₂Fe(OAc)₂·59H₂O
 (CH₃COOC)₂Fe(OAc)₃·59H₂O
 (CH₃COOC)₂Fe(OAc)₂·60H₂O
 (CH₃COOC)₂Fe(OAc)₃·60H₂O
 (CH₃COOC)₂Fe(OAc)₂·61H₂O
 (CH₃COOC)₂Fe(OAc)₃·61H₂O
 (CH₃COOC)₂Fe(OAc)₂·62H₂O
 (CH₃COOC)₂Fe(OAc)₃·62H₂O
 (CH₃COOC)₂Fe(OAc)₂·63H₂O
 (CH₃COOC)₂Fe(OAc)₃·63H₂O
 (CH₃COOC)₂Fe(OAc)₂·64H₂O
 (CH₃COOC)₂Fe(OAc)₃·64H₂O
 (CH₃COOC)₂Fe(OAc)₂·65H₂O
 (CH₃COOC)₂Fe(OAc)₃·65H₂O
 (CH₃COOC)₂Fe(OAc)₂·66H₂O
 (CH₃COOC)₂Fe(OAc)₃·66H₂O
 (CH₃COOC)₂Fe(OAc)₂·67H₂O
 (CH₃COOC)₂Fe(OAc)₃·67H₂O
 (CH₃COOC)₂Fe(OAc)₂·68H₂O
 (CH₃COOC)₂Fe(OAc)₃·68H₂O
 (CH₃COOC)₂Fe(OAc)₂·69H₂O
 (CH₃COOC)₂Fe(OAc)₃·69H₂O
 (CH₃COOC)₂Fe(OAc)₂·70H₂O
 (CH₃COOC)₂Fe(OAc)₃·70H₂O
 (CH₃COOC)₂Fe(OAc)₂·71H₂O
 (CH₃COOC)₂Fe(OAc)₃·71H₂O
 (CH₃COOC)₂Fe(OAc)₂·72H₂O
 (CH₃COOC)₂Fe(OAc)₃·72H₂O
 (CH₃COOC)₂Fe(OAc)₂·73H₂O
 (CH₃COOC)₂Fe(OAc)₃·73H₂O
 (CH₃COOC)₂Fe(OAc)₂·74H₂O
 (CH₃COOC)₂Fe(OAc)₃·74H₂O
 (CH₃COOC)₂Fe(OAc)₂·75H₂O
 (CH₃COOC)₂Fe(OAc)₃·75H₂O
 (CH₃COOC)₂Fe(OAc)₂·76H₂O
 (CH₃COOC)₂Fe(OAc)₃·76H₂O
 (CH₃COOC)₂Fe(OAc)₂·77H₂O
 (CH₃COOC)₂Fe(OAc)₃·77H₂O
 (CH₃COOC)₂Fe(OAc)₂·78H₂O
 (CH₃COOC)₂Fe(OAc)₃·78H₂O
 (CH₃COOC)₂Fe(OAc)₂·79H₂O
 (CH₃COOC)₂Fe(OAc)₃·79H₂O
 (CH₃COOC)₂Fe(OAc)₂·80H₂O
 (CH₃COOC)₂Fe(OAc)₃·80H₂O
 (CH₃COOC)₂Fe(OAc)₂·81H₂O
 (CH₃COOC)₂Fe(OAc)₃·81H₂O
 (CH₃COOC)₂Fe(OAc)₂·82H₂O
 (CH₃COOC)₂Fe(OAc)₃·82H₂O
 (CH₃COOC)₂Fe(OAc)₂·83H₂O
 (CH₃COOC)₂Fe(OAc)₃·83H₂O
 (CH₃COOC)₂Fe(OAc)₂·84H₂O
 (CH₃COOC)₂Fe(OAc)₃·84H₂O
 (CH₃COOC)₂Fe(OAc)₂·85H₂O
 (CH₃COOC)₂Fe(OAc)₃·85H₂O
 (CH₃COOC)₂Fe(OAc)₂·86H₂O
 (CH₃COOC)₂Fe(OAc)₃·86H₂O
 (CH₃COOC)₂Fe(OAc)₂·87H₂O
 (CH₃COOC)₂Fe(OAc)₃·87H₂O
 (CH₃COOC)₂Fe(OAc)₂·88H₂O
 (CH₃COOC)₂Fe(OAc)₃·88H₂O
 (CH₃COOC)₂Fe(OAc)₂·89H₂O
 (CH₃COOC)₂Fe(OAc)₃·89H₂O
 (CH₃COOC)₂Fe(OAc)₂·90H₂O
 (CH₃COOC)₂Fe(OAc)₃·90H₂O
 (CH₃COOC)₂Fe(OAc)₂·91H₂O
 (CH₃COOC)₂Fe(OAc)₃·91H₂O
 (CH₃COOC)₂Fe(OAc)₂·92H₂O
 (CH₃COOC)₂Fe(OAc)₃·92H₂O
 (CH₃COOC)₂Fe(OAc)₂·93H₂O
 (CH₃COOC)₂Fe(OAc)₃·93H_{2</}

also available as L- or any group having in its structure two, three, or four unshared electrons, with the condition that only one electron is shared per metal M. Examples of such groups are CrH₆, SiAs₂, SiP₂, GeP₂, Sb₂, S₂, S₃, S₄, and S₆. It can be any ester from the Periodic Groups VB, VIB, VIIB, and VIIIIB, such as, for example, Ti-Fe-V-Al, Fe-Cr-Al, Ti-Pt, Fe-Pt, Co-Pt, Ni-Pt and Pt.

and in this situation should the substances to initiate polymerization of the monomers or precursors (i.e. a hydroperoxide, anhydride, ester, etc.) be added under the desired conditions. Such measure generally will be in the range of 0.1 to 2.0 weight percent, and productivity 0.1 to 10.0 weight percent, based on the weight of curable monomer.

The differentiation of the two main types of mechanisms of sensory transduction is determined from the two different types of receptors. The first type of receptor, the mechanoreceptor, uses the mechanical energy of the environment to produce a signal. The second type of receptor, the chemoreceptor, uses the chemical energy of the environment to produce a signal.

bound by one photon can ultimately lead to the production of two organometallic-derived species and two free radical initiators. It should be noted that competing or secondary photoprocesses, such as dissociation of a carbonyl bond, can occur. Such processes however, occur in such a manner as to such an extent that the active catalytic species and initiator are still produced so as to effect curing of the composition.

Solvents, preferably organic, can be used to assist in dissolution of the curing agent in the ethylenically-unsaturated monomer, the polyurethane precursors, or the epoxy monomer, and as a processing aid.

Representative solvents include acetone, methyl ethyl ketone, cyclopentanone, methyl cyclohexane acetone, methyl chloride, nitroethane, methyl formate, acetonitrile, gamma-butyrolactone, and 1,2-dimethylbenzene (pymex). In some applications, it may be advantageous to add the curing agent onto an inert support such as silica, alumina, clay, etc., as described in U.S. Patent No. 4,871,317.

For those compositions of the invention which are radiation-sensitive, i.e., the compositions containing ethylenically-unsaturated monomers, epoxy monomer, or polyurethane precursors and as curing agent as a combination of an organometallic compound of Formula I and an organ salt of Formula II, any source of radiation including electron beam radiation and radiation in the ultraviolet and visible region of the spectrum (e.g., about 200 to 800 nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arcs, tungsten lamps, xenon lamps, lasers, sunlight, etc. The required amount of radiation to effect polymerization is dependent upon such factors as the nature and concentrations of the organometallic compound and organ salt, the particular ethylenically-unsaturated monomer, polyurethane precursors, or epoxy monomer, the thickness of the exposed material, type of substrate, intensity of the radiation source and amount of heat associated with the radiation.

Thermal polymerization using direct heating or infrared electromagnetic radiation, as is known in the art, can be used to cure ethylenically-unsaturated or polyurethane precursors according to the teachings of the

It is within the scope of this invention to include two-stage polymerization (curing). By first activating the curable compositions and subsequently thermally curing the activated precursors so obtained, the reaction temperature employed for the subsequent heat-curing. These activated precursors may normally be cured at temperatures which are substantially lower than those required for the direct thermal curing, with an advantage in the range from 50 to 100° C.

110°C. The two-stage curing and mixing is possible in curing and polymerization of the monomer and advantageous manner.

Advantages such as solvents, pigments, abrasive granules, stabilizers, amorphous, non-agents, bodying agents, filling agents, colorants, inert fillers, binders, coloring agents, fungicides, defoamers, surfactants, plasticizers, and other additives as known to those skilled in the art can be added to the compositions of this invention. These can be added in an amount effective for their intended purpose.

Compositions of this invention are useful for coatings, foams, shaped articles, adhesives, filled or reinforced composite, abrasives, caulking and sealing compounds, casting and molding compounds, potting and encapsulated compounds, impregnating and coating compounds, and other applications which

are known to those skilled in the art.

Compositions of the invention may be applied, preferably as a liquid, to a substrate such as aluminum, copper, cadmium, zinc, glass, paper, wood, or various plastic items such as polyisobutylene, polyacrylate, polyvinylchloride, polycyanoacrylate, poly(methylmethacrylate), and the like, and exposed to ultraviolet light. The compositions of the invention may be used in the production of part of the coating, by irradiation through a mask, those sections which have not exposed may be washed with a solvent to remove the unpolymerized portions while leaving the photopolymerized, insoluble portions in place. Thus, components of the invention may be used in the production of articles useful in the graphic arts such as printing plates and printed circuits. Methods of producing printing plates and printed circuits from photopolymerizing compositions also well known in the art.

Optical and electronic methods of detection are further illustrated by the following examples. As well as other conditions and details particular materials and amounts thereof recited in these examples, as well as other conditions and amounts thereof recited in these examples, all parts are parts by weight unless indicated otherwise. All examples were prepared in ambient atmosphere (presence of oxygen) and under

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EXAMPLE 1

the stock solution. The sample was photocured to a solid using a Kodak Tu Carousal TU projector in 12 minutes.

Three samples were prepared as above, except the iron dimer and cobaltum salt were added as follows: sample (a), 0.01 g [CoFe(CO)₃]₂; 0.03 g Ph₃P₁⁻; sample (b), 0.01 g [CoFe(CO)₃]₂, 0.03 g Ph₃P₁⁻; sample (c) was left in the dark while samples (b) and (c) were irradiated as above. None of the three samples showed evidence of any curing, no obvious change in evidence, after 20 minutes.

EXAMPLE 4

This example illustrates the use of an organometallic compound containing a transition metal-carbon single bond in the curing agent to photocatalyze the formation of polyurethane. 0.52 g Diamodur W (1,1-methylene bis(cyclohexyl isocyanate)) and 0.72 g Carbosilane 400 (tobol) were combined and added to 0.01 g CoPh(CH₃)₂ (Co = 1,1'-bis(cyclohexyl isocyanate)) which had been dissolved in 0.15 ml of a mixture CH₂Cl₂ and gamma-butyrolactone. The resulting mixture was irradiated with a Hanovia 1640 watt medium pressure mercury arc lamp through Pyrex. Complete cure was achieved within 12 minutes irradiation time.

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TABLE I

Characterization of Compounds				
Elemental Analysis (Report/Calculated)				
Compound	%C	%H	Melting Point, C	
CoFe(CO) ₃ SnPh ₃	57.05/5.0	1.80/0.8	135-136	
CoFe(CO) ₃ GaPh ₃	62.36/2.4	4.24/2	159-160	
CoFe(CO) ₃ Li ₂ SnPh ₃	49.74/0.8	3.33/0.2	146-148	
(CO) ₃ AlSnPh ₃	51.05/0.7	2.82/0.8	146-149	
(CO) ₃ MgBrPh ₃	39.9/30.8	1.61/1.5	138-139	
(CO) ₃ RbSnPh ₃	52.6/32.5	3.4/3.4	213-214	

This example illustrates the photocuring of polyurethane precursors to polyurethane in the presence and absence of O₂ using transition metal-transition metal bond containing organometallic compounds and organum salt as curing agent.

A mixture of 10 mg [CoFe(CO)₃]₂, 30 mg Ph₃P₁⁻, 0.27 g Diamodur W (1,1-methylene bis(cyclohexyl isocyanate)), and 117 g polyethylenglycol (M.P. v = 400) was directed in W (1,4-methanobis(bis(4-phenylene isocyanate))), and 117 g polyethylenglycol (M.P. v = 400) was directed in half, one half was bubbled with N₂ for 2-3 minutes, the other left open to the atmosphere. Both samples were irradiated simultaneously with the output of a 450 watt Hanovia mercury lamp, filtered through Pyrex and a water infrared filter. Both samples cured after 100 minutes irradiation. T = demonstrates IR in the presence of organum salt curing occurs with or without O₂ present.

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EXAMPLE 5

This example illustrates the photocuring of acrylate precursors using transition metal-transition metal bond containing organometallic compounds and organum salts. A stock solution was prepared from 7 organometallic compounds and iodonium and sulfonium salts. Samples were prepared as in Example 3 using 1/25 g of the stock solution, 0.01 g neutral metal-bonded compound and 0.015 g Ph₃P₁⁻ in 0.05 g gamma-butyrolactone. Irradiations were carried out on a 450 W Hanovia medium pressure mercury arc through Pyrex. Alternatively, these compositions can be cured thermally.

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EXAMPLE 2

Several organometallic compounds were prepared according to literature methods. CoW(CO)₃CH₃ was prepared according to the method of F.S. Paper, G. Waterman, Inorg. Nucl. Chem., 1956, 3104-124. (CoW(CO)₃CH₃ was prepared according to the method of R. Birdstone, J.R. Melling, J. Organomet. Chem. 1978, 157, 238. CoFe(CO)₃SnPh₃ was prepared according to the method of G. Carrelle, E. Colomer, P. Duriv, W.E. Douglas, J. Organomet. Chem., 1977, 135, 373, 388. The method of J. P. Bélier, A. Woicik, J. Amer. Chem. Soc., 1955, 77, 4822 was used to prepare CoFe(CO)₃SnPh₃, and that of R. B. King, M. B. Bassett, J. Organomet. Chem., 1964, 2, 15-37, to prepare CoFe(CO)₃SnPh₃. The preparation of Ph₃P₁⁻ has been described in U.S. Patent No. 4,800,464. These compounds are used in subsequent examples.

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EXAMPLE 3

This example illustrates the use of an organometallic compound containing a transition metal-transition metal bond in the curing agent to photocatalyze the formation of polyurethane. A stock solution of 4,4'-methylenebis(cyclohexyl isocyanate) (Diamodur W, a Mobay Corp., Pittsburgh, PA) and 1,1'-methanobis(cyclohexyl isocyanate) (Carbosilane 400, Union Carbide, Danbury, CT) was prepared. To a mixture of Ph₃P₁⁻ and 0.02 g Ph₃P₁⁻ in 0.1 g gamma-butyrolactone was added 1/25 g of

TABLE

Iodination and Substitution Sets	Cure time, minutes	Ph_3P^+ - Pi_3^-	Ph_3S^+ - Pi_3^-
Organometallic compound			
$(\text{C}_6\text{H}_5\text{CO})_3\text{I}$	6.0	> 100	
$(\text{C}_6\text{H}_5\text{CO})_2\text{Fe}(\text{C}_6\text{H}_5)_2\text{I}$	8.0	20-25	
$(\text{C}_6\text{H}_5\text{CO})_2\text{Fe}(\text{C}_6\text{H}_5)_2\text{I}$	12-15	7-12	
$(\text{C}_6\text{H}_5\text{CO})_2\text{Fe}(\text{C}_6\text{H}_5)_2\text{I}$	20-40	20-40	
$\text{Cu}(\text{C}_6\text{H}_5\text{CO})_2\text{I}$	40-65	55-65	
$(\text{C}_6\text{H}_5\text{CO})_2\text{Fe}(\text{C}_6\text{H}_5)_2\text{I}$	55-67	60-65	
$\text{Fe}(\text{C}_6\text{H}_5\text{CO})_3$	about 65		

This procedure yields examples of two-component curing agents wherein organometallic compounds contain trivalent metal-crown entities which are effective in the curing agent for polyurethane precursors. A stock solution of polyurethane precursor was prepared by mixing 21.0 Decadur W and 32.0 g Carbopol 400 and stirring until before use. Samples were prepared by dissolving 10 mg catalyst and 20 mg Dicumyl Phthalate in 0.2 g $\text{Cr}(\text{Cl}_3)_6$. 2.0 stock solution was added in the Dicumyl Phthalate premixtures of 100 g in 0.2 g $\text{Cr}(\text{Cl}_3)_6$. 2.0 stock solution was added under the lamp until 10 min. The temperature of samples under the lamp reached ca. 50°C within 10 min. The time to a viscosity increase is noted in Table III, and "Cure time" is the time for a sample to become as viscous as the samples become after 30 min irradiation, within 30 min irradiation. The sample becomes more viscous as the irradiation continues.

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Count of Licensee Procurers	Case Period, min		20 partial partial partial	20 partial partial partial
	Vacancy	Crimes		
Capital	Capital + Vacancy	Capital + Vacancy	Capital + Vacancy + Partial	Capital + Vacancy + Partial

The data show clearing occurs with or without edetate sodium salts. In some cases, adventitious oxygen can provide a suitable clearing agent. However, the use of edemate salts is preferred since it is much easier to control the drug release/bioavailability and cost.

Example 8

This example describes the use of the curing agent containing an organonitroso compound containing a transition metal-carbon bond to cure epoxies. Each sample was prepared by dissolving 10 mg catalyst and 20 mg diphenylmethane diisocyanate (40 wt-%) in 0.2 g CH_2Cl_2 . 2.0 g cyclohexane diol was added in the dark, and samples were then irradiated under a Hg-254 Quartz UV lamp until formation of polymer was tested by placing a few drops of the sample in about 2 ml methanol. Formation of precipitate indicated that polymer had formed. Further polymerization resulted in a viscosity increase in the sample. Figures are indicated in Table IV.

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Curing Agent	Precipitate formed, min.	Vacancy increased min
Copraolin Copraolin + iodine	no cure	no cure
$\text{Ca}(\text{C}_2\text{O}_4)_{2}\text{H}_2\text{O}$ + iodine	3.5	30
(PhenylPhenylMethane) + PPi + $\text{Ca}(\text{C}_2\text{O}_4)_{2}\text{H}_2\text{O}$	3	30
$\text{Ca}(\text{C}_2\text{O}_4)_{2}\text{H}_2\text{O}$ + iodine	2	no further cure
$\text{Ca}(\text{C}_2\text{O}_4)_{2}\text{H}_2\text{O}$ + iodine	2	30

a includes for purposes of comparison.

EXAMPLE 8

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TABLE V

Compound	Photocatalysis of Epoxy Cure	
	Cure Time*	Oxidum Salt Added
ICOFnCOH _n b	>10	-
CofnCOH _n SuPh _n	>10	5
CofnCOH _n Gem _n	>10	5
ICOFnCOH _n b SuPh _n	>10	3
Mn(IV)O ₄	>10	-
(CO ₂ H) _n Me _n	>10	4
(CO ₂ H) _n Me _n SuPh _n	1	3
Pe _n CO ₂ H _n	6	1.5
CofnCOH _n SuPh _n	4	-

* min. in minutes to cure.

EXAMPLE 10

To further demonstrate the activity of the curing agent, a series of experiments were carried out in another epoxy and/or acrylate composition. The organometallic compound, with and without the oxidum salt, was photopolymerized in presence of an epoxy or acrylate. The specific system used is as follows: methyl acrylate was distilled from hydroquinone and stored cold until ready for use. Cyclohexane oxide was used as solubility from Aldrich. The organometallic compounds were obtained from commercial sources. Dicyanohydrazinodiphenylphosphine was recrystallized from acetone/propenol. All experiments were done at 100% solids, except as noted.

In a small well with pieces of 0.02 g of the organometallic compound and about 0.04 g of the isolobium salt along with 2.0 g of the desired monomer. For the acrylate tests, the solutions were purged with N₂ for 60 sec before and continuously during the photolysis. The epoxy tests were performed without purging, well down to the air. The light source was one 15 watt daylight fluorescent bulb. In Table VI below, the cure times represent the time required to reach the same degree of cure, usually gelation of the solution. Alternatively, the compositions can be cured thermally.

TABLE V

Catalyst System	Photocatalyzed Cure Times of Epoxy and Acrylate Compositions	
	Epoxy	Acrylate
(CofnCOH _n) ₂ / Isolobium	>200	>200
Mn(IV)O ₄	>200	>200
Mn(IV)O ₄ / Isolobium	>200	>200
Pe _n CO ₂ H _n / Isolobium	>200	>200
Co _n CO ₂ H _n	>200	>200
Co _n CO ₂ H _n / Isolobium	>200	>200
Co _n CO ₂ H _n / CuSO ₄ / Isolobium	>200	>200

a Cure time in seconds.

b Not done.

c Recorded in the dark using existing
d 10% by wt. gamma-irradiation dose.EXAMPLE 11

This example demonstrates the ability of isolobium methacrylate and Mn(IV)O₄ from organometallic compounds to photocatalyze the cure of diphenylmethacrylate compounds in the presence of isolobium salt. The salts were carried out in the following manner: Into a glass vial were weighed out 0.05g of the claimed organometallic compound and 0.10g diphenylmethacrylate (DPM) (Aldrich Company, recrystallized from acetone/propenol). Then, the following amounts were added and under subdued light: 0.2g of gamma-stabilizer (Aldrich Chemical Company), 5.0g methyl acrylate (Aldrich Chemical Company), 5.0g of pentamethylbenzene (Aldrich, Chemours Company) were added to prepare the coating solution. The solutions were coated onto 70 micrometers (1 mil) polypropylene substrate (Allied Company) using a #22 wire screen mesh. The sample coatings were developed with a second sheet of polyester and exposed to two 15 watt Schott 420 nm ultraviolet light at a distance of 2 cm. The time required to produce a monely cured coating was recorded. Under the conditions of this test, the diphenylmethacrylate alone requires greater than 10 min to cure.

TABLE VI

Curing of Ethylenically Unsaturated Monomers Organometallic Compound	Cure Time ^a	
	No Catalyst Added	Catalyst Added
(C ₆ H ₅ CO) ₂ b	>600	15
C ₆ H ₅ CO ₂ Na ^c PF ₆	>600	120
C ₆ H ₅ CO ₂ Na ^c PF ₆	>600	120
(C ₆ H ₅ CO) ₂ SiPh ₃	>600	60
Mn ^d (CO) ₅	>600	<15
(CO ₂) ₂ Mn ^d BF ₄	300	300
(CO ₂) ₂ Mn ^d PF ₆	60	30
Mn ^d (CO) ₅	120	60
(C ₆ H ₅ CO) ₂ SiPh ₃	>600	30
(C ₆ H ₅ CO) ₂ SiPh ₃	>600	240

^a Little or seconds to cure.^b Saturated solution, <0.01g dissolved.EXAMPLE 12

Further examples of the curing of ethylenically unsaturated monomer (25 g of pentenylthiobenzene) or epoxy monomer (cyclohexane oxide) are provided here. A curable composition consisting of 0.01g of the organometallic compound or 0.02g of diphenyltinobutin hexaphosphinate or twice same amounts of both compounds added to either *r*-monomer. The light source used was for UV exposure, about 300 nm, two 15 watt G.E. daylight bulbs and/or the visible, a Kodak Carousel Projector or the projector with a 440 nm filter. The initiation of polymerization was detected by solution gelation for the acrylic and for the epoxy the precipitation of the polymer from a 2% ammonium sulfate solution. Free radical systems were purged with N₂ for 2 minutes before and continuously during irradiation while the catalytic samples were left open to the air without purging. Sample sizes 0.5 to 2 to 3 ml. in a 13 x 100 mm Pyrex test tube. The results of these tests are shown in Table VII.

TABLE VII

Curing of Ethylenically Unsaturated Monomers Organometallic Compound	Photocatalyzed Cure Times of Epoxy and Acrylic Compositions ^a	
	Curing Agent	Epoxy
(C ₆ H ₅ CO) ₂ b	10 ^b	>10 ^c
(C ₆ H ₅ CO) ₂ SiPh ₃	60 ^b	>5 ^c
(C ₆ H ₅ CO) ₂ SiPh ₃	10 ^b	<10 ^c
Mn ^d (CO) ₅	10 ^b	>300 ^c
Mn ^d (CO) ₅	10 ^b	>300 ^c
Mn ^d (CO) ₅	10 ^b	<10 ^c
Mn ^d (CO) ₅	10 ^b	<10 ^c

^a Cure times given in seconds.^b Unfiltered projector as light source.^c The diphenyltinobutin salt showed no indication of polymerization by visual means under these same conditions.^d 440 nm filter used with the projector.^e Blockade used as the light source, ca. 300 nm.EXAMPLE 13

Examples of the photocuring of ethylenically unsaturated monomers using transition metal-boron metal bond containing organometallic compounds and adducts are given here. Samples were prepared as 1.0 g methyl acrylate containing 0.01 g metal-metal bond containing complex and 0.015 g Phn^fPF₆. Up to 0.05 g borophotocatalysts of methanesilane chloride were used to decrease the photocatalyst systems. Samples were bubbled with N₂ and irradiated using a Kodak Carousel slide projector, with a 300 nm cutoff filter, and the time required to cure the sample recorded in Table XI. Alternatively, the compositions can be cured thermally.

TABLE IX

Compound and Phn ^f PF ₆	Curing of Ethylenically Unsaturated Monomers		
	Conditions	Cure Time	
(C ₆ H ₅ CO) ₂ b	unad.	30 sec. slow dark reaction	
Mn ^d (CO) ₅	unad.	30 sec. no dark reaction	
(C ₆ H ₅ CO) ₂ SiPh ₃	unad.	40 sec. no dark reaction	
[Phn ^f CO] ₂ b	unad.	6 min. no dark reaction	
Cd(CO) ₄	unad.	Minutes, slow dark reaction	
Cd(CO) ₄	dark	Cure during decomposition	

EXAMPLE 14

This example describes the curing of ethylenically-unsaturated monomers with transition metal-boron bonded organometallic compounds. Each sample was prepared by dissolving 10 mg catalyst and 20 mg

PF_1 = mole ratio for potassium stannous dimer = 21; NOOCOCH_3 = 1.0, weight %, iron dinner = 0.0%, sodium salt = 1.2%. Samples were irradiated simultaneously using 300 nm BulbF_1 bulbs (115 watts for 10 min., then analyzed by 400 MHz ^1H nuclear magnetic resonance spectroscopy. Concentrations and losses in Table XIX.

TABLE XIX

Dual Curing of Polyurethane Precursors and Epoxy-Functionalized Monomers		Concen to Polymer
Ornithine Salt	Condition	
Phenyl	dark	4%
Phenyl	irradiation, deoxygenated	50%
Phenyl	dark	75%
None	irradiation, deoxygenated	0%
None	dark	20%
None	irradiation, deoxygenated	75%
None	dark	10%

- a. Polyurethane precursors are from a stock solution consisting of 23.1 g of Desmodur TM W and 32.6 g of Carbowax 400. Cure times are followed by an indication in parentheses of extent of cure, where V = viscous, WV = very viscous, S = solid.

b. Monomer is cyclobutene oxide, purified by distillation. Cure time is defined as the time necessary to observe formation of precipitate when one drop of sample is placed in 2 mL of methanol.

c. Monomer is methyl acrylate, purified prior to use by distillation under reduced pressure. After sonication addition but before irradiation, samples were deoxygenated by bubbling a stream of nitrogen gas through the solution for 2 min, with care being taken to prevent any light from reaching the sample during oxygenation. Cure is defined by an increase in solution viscosity or a sudden exotherm indicating rapid polymerisation (also accompanied by a sudden increase in viscosity).

d. Included for purposes of comparison to data in other tables.

e. 60 min irradiation with Carousel Projector, followed by 60 minutes of irradiation in room (fluorescent) light.

f. This particular combination was not tested.

g. 30 minutes irradiation with Kodak projector, following by 30 minutes irradiation under a Banovia Quartz Utility Lamp (6 inches from bulb), followed by sample storage/irradiation in room (fluorescent) light.

- h. Irradiation with Banovia Quartz Utility Lamp (15 cm from bulb) in place of the Kodak Projector.
- i. 60 min irradiation with a 400 W GE incandescent bulb.
- j. None determined in the lab.

EXAMPLE 18 (comparative)

This example demonstrates simultaneous curing of epoxycyanohexane monomer and ornithine. Curing times will not show that both monomers have reacted at the same time. It is possible to use nuclear magnetic resonance spectroscopy to determine the two polymeric in the presence of each other. The experiment was carried out in the following manner: A 10.0 wt. percent mixture of epoxycyanohexane and cyanohexane dodecylbenzenesulfonate (0.025 g) with the benzidine 0.025 g with the monomers (diamine) in the specified amounts of both compounds. In a small vial were placed 2 mL of the sample and it was purged for 1 min before and continually during irradiation. The light source was a 10 watt G.E. incandescent bulb. Irradiation time was 2 minutes. Immediately after completion of the photopolymerization, the sample in CDCl_3 was taken. The amount of polymerization was determined by the ratio of the peak intensity of the monomer to that of polymer phos. monomer. The results of the study are shown in Table XX.

TABLE XX

Percent Conversion to Polymer from Stock Sample ^a	
Curing Agent	Epoxide
CpFeCOOEt_2	0
CpFeCOOEt_2 /Benzidine	25
Benzidine	15
MnFeCOOEt_2	45
MnFeCOOEt_2 /Benzidine	37

EXAMPLE 17 (comparative)

This example illustrates the dual curing of epoxycyanohexane and ornithine-urethane monomers using the curing agent CpFeCOOEt_2 / PdCl_2 / PF_1 . Samples 1.25 g in size, were prepared from stock solutions of 200 parts Desmodur W (4.4% methyl acrylate/cyanohexane copolymer), 2.52 parts polyhydroxyethanol (MW = 400), 5.0 parts methyl acrylate (freshly distilled), and 0.02 parts CpFeCOOEt_2 . To half of the stock solution was added 0.02 parts PdCl_2

^a Starts with an 8.00 mole monomer.
^b None determined in the lab.

As can be seen from the table results, the system effectively converts both epoxide and urethane polymerization simultaneously.

EXAMPLE 19 (comparative)

This example demonstrates the simultaneous curing of ethylenically unsaturated and epoxy monomers. The curable composition consists of methyl acrylate, cyclohexene oxide and gamma-butyrolactone. 1.0 g gamma-butyrolactone, 5.0 g methyl acrylate and 5.0 g cyclohexene oxide. Depending on the test effect^a to be made 0.05 g of the desired organometallic compound and/or 0.1 g dichlorodimethyl boronophosphate. A 3 g portion of this composition was placed in a glass vial and irradiated between two 15 watt G.E. daylight fluorescent bulbs using an Ultraviolet Products lamp holder (lamp separation distance 4 cm). The sample was purged with nitrogen for one minute preceding and immediately during photopolymerization. The irradiation time required to produce a polymer insoluble in chlorobenzene is recorded and is noted in Table XIV.

All monomers were distilled before use; methyl acrylate and glycidyl acrylate from hydroquinone. Sample irradiations were carried out under subdued light. The polymerizable mixture consisted of 0.2 g gamma-butyrolactone, 1.0 g glycidyl acrylate, 5.0 g methyl acrylate and 5.0 g cyclohexene oxide. Depending on the test effect^a to be made 0.05 g of the desired organometallic compound and/or 0.1 g dichlorodimethyl boronophosphate. A 3 g portion of this composition was placed in a glass vial and irradiated between two 15 watt G.E. daylight fluorescent bulbs using an Ultraviolet Products lamp holder (lamp separation distance 4 cm). The sample was purged with nitrogen for one minute preceding and immediately during photopolymerization. The irradiation time required to produce a polymer insoluble in chlorobenzene is recorded and is noted in Table XIV.

Alternately these compositions can be cured thermally.

TABLE XIV

Compound	Cure Time*	
	No Ormiston Salt Added	Ormiston Salt Added
[GeFe(CO) ₃] ₂ b	>15	1
CeFe(CO) ₃ SnPh ₃	>15	10
CeFe(CO) ₃ GaPh ₃	>15	15
[GeFe(CO) ₃] ₂ SnPh ₃	>15	10
Mn(CO) ₅ c	>15	1.5
Fe(CO) ₅ SnPh ₃	>15	10
Fe(CO) ₅ SnPh ₃	>10	4
Re(CO) ₅	>10	5
[GeAl(CO) ₃] ₂ b	>15	1.5
CoAl(CO) ₃ SnPh ₃	>15	10

*Time in minutes to produce insoluble crosslinked system.

Dichlorodimethyl boronophosphate alone under these conditions did not produce a crosslinked system after 15 minutes.

b Only 0.01 g of this compound was used.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of the invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

Claims

1. A polymerizable composition comprising one class of polymeric precursors selected from the group consisting of 1) at least one ethylenically-unsaturated monomer, 2) at least one epoxy monomer, and 3) not to be unduly limited to 4) inorganic endotherms set forth herein.

a and optionally a solvent

2. The composition according to claim 1 which is photo-polymerizable

3. The composition according to claim 1 wherein said class of polymeric precursors is at least one ethylenically-unsaturated monomer or polyurethane precursors and said composition is thermally polymerizable.

4. The composition according to claims 1 to 3 wherein said organometallic compound has the formula:

$$L_1 L_2 M$$

L₁ represents none, or 1 to 12 ligands contributing p-orbitals that can be the same or different ligands

10 selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each containing 2 to 24 π -electrons to the valence shell of M.

L₂ represents none, or 1 to 24 ligands that can be the same or different contributing an even number of sigma-electrons selected from mono-, di-, and tri-dentate ligands, each containing 2, 4, or 6 sigma-electrons

15 to the valence shell of M.

L₃ represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron each to the valence shell of each M.

Ligands L₁, L₂, and L₃ can be bridging or non-bridging ligands.

5. The composition according to claims of Periodic Groups IVB and VB, VIB, VIIB, and VIIIB, with the proviso that said organometallic compound contains at least one of a meta-metal sigma bond and L₁, and L₂ are chosen so as to achieve a stable configuration.

6. The composition according to claims 1 to 4 wherein said organometallic compound has the formula:

$$A X$$

wherein A is an iodide, sulfide, sulfonium cation, and X is an organic sulfonate counterion, or a halogenated metal or metalloid counterion.

7. The composition according to claim 1 to 4 of the same or different metal atom selected from the group selected from the group consisting of acetylides, carbynes and vinyl compounds.

8. A process comprising the steps of:

a) providing a polymerizable composition according to claims 1 to 7, and
b) allowing said mixture to polymerize or adding energy to said mixture to effect polymerization.

9. A layered structure comprising a substrate having coated on one surface thereof the polymerizable composition according to claim 1 to 7.

10. The layered structure according to claim 9 which is an integrable structure.

11. The polymerizable composition according to claims 1 to 7 and 9 which has been cured.

12. A shaped article according to claim 11.